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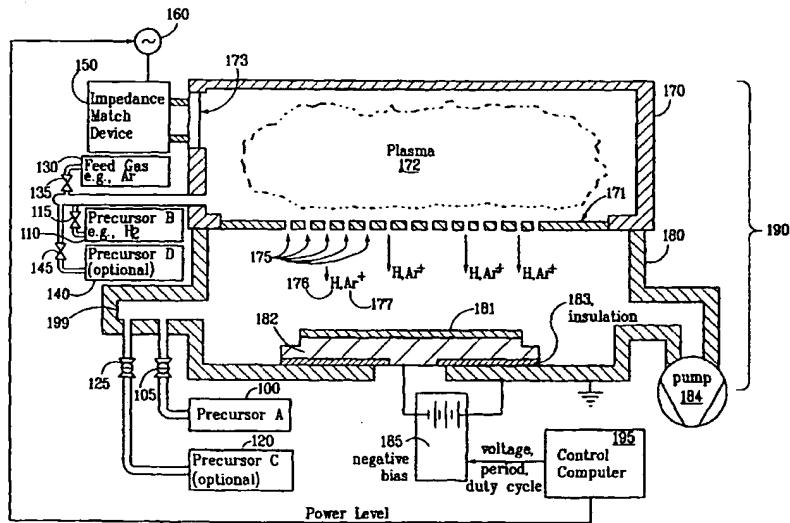
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(54) Title: SYSTEM AND METHOD FOR MODULATED ION-INDUCED ATOMIC LAYER DEPOSITION (MI-ALD)



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(57) Abstract: The present invention relates to an enhanced sequential or non-sequential atomic layer deposition (ALD) apparatus and technique suitable for deposition of barrier layers, adhesion layers, seed layers, low dielectric constant (low-k) films, high dielectric constant (high-k) films, and other conductive, semi-conductive, and non-conductive films. This is accomplished by providing a non-thermal or non-pyrolytic means of triggering the deposition reaction; providing a means of depositing a purer film of higher density at lower temperatures; providing a means of modulating the deposition sequence and hence the overall process rate; and providing a means of improved radical (176) generation and delivery.



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## Specification

### 1    Cross-Reference to Related Applications

2        This application claims the benefit of U.S. Provisional Application Nos.  
3        60/251,795, and 60/254,280, both filed December 6, 2000, as well as U.S.  
4        Utility Application Nos. 09/812,285, 09/812,352, and 09/812,486, all filed  
5        March 19, 2001, and U.S. Utility Application No. 09/854,092, filed May 10,  
6        2001.

### 7    Background of the Invention

8        The present invention relates generally to the field of advanced thin  
9        film deposition methods commonly used in the semiconductor, data storage,  
10       flat panel display, as well as allied or other industries. More particularly, the  
11       present invention relates to an enhanced sequential or non-sequential atomic  
12       layer deposition (ALD) apparatus and technique suitable for deposition of  
13       barrier layers, adhesion layers, seed layers, low dielectric constant (low-k)  
14       films, high dielectric constant (high-k) films, and other conductive, semi-  
15       conductive, and non-conductive thin films.

16       The disadvantages of conventional ALD are additionally discussed in a  
17       copending application with the same assignee entitled "Method and  
18       Apparatus for Improved Temperature Control in Atomic Layer Deposition",  
19       which is hereby incorporated by reference in its entirety and may be found as  
20       copending provisional, Application No. 09/854,092.

21

1    **Brief Description of the Prior Art**

2           As integrated circuit (IC) dimensions shrink and the aspect ratios of the  
3           resulting features increase, the ability to deposit conformal, ultra-thin films on  
4           the sides and bottoms of high aspect ratio trenches and vias becomes  
5           increasingly important. These conformal, ultra-thin films are typically used  
6           as "liner" material to enhance adhesion, prevent inter-diffusion and/or  
7           chemical reaction between the underlying dielectric and the overlying metal,  
8           and promote the deposition of a subsequent film.

9           In addition, decreasing device dimensions and increasing device  
10          densities has necessitated the transition from traditional CVD tungsten plug  
11          and aluminum interconnect technology to copper interconnect technology.

12          This transition is driven by both the increasing impact of the RC interconnect  
13          delay on device speed and by the electromigration (i.e., the mass transport of  
14          metal due to momentum transfer between conducting electrons and diffusing  
15          metal atoms, thereby affecting reliability) limitations of aluminum based  
16          conductors for sub 0.25  $\mu\text{m}$  device generations. Copper is preferred due to its  
17          lower resistivity and higher (greater than 10 times) electromigration resistance  
18          as compared to aluminum. A single or dual damascene copper metallization  
19          scheme is used since it eliminates the need for copper etching and reduces the  
20          number of integration steps required. However, the burden now shifts to the  
21          metal deposition step(s) as the copper must fill predefined high aspect ratio  
22          trenches and/or vias in the dielectric. Electroplating has emerged as the  
23          copper fill technique of choice due to its low deposition temperature, high  
24          deposition rate, and potential low manufacturing cost.

1        Two major challenges exist for copper wiring technology: the barrier  
2    and seed layers. Copper can diffuse readily into silicon and most dielectrics.  
3    This diffusion may lead to electrical leakage between metal wires and poor  
4    device performance. An encapsulating barrier layer is needed to isolate the  
5    copper from the surrounding material (e.g., dielectric or Si), thus preventing  
6    copper diffusion into and/or reaction with the underlying material (e.g.  
7    dielectric or Si). In addition, the barrier layer also serves as the adhesion or  
8    glue layer between the patterned dielectric trench or via and the copper used  
9    to fill it. The dielectric material can be a low dielectric constant, i.e. low-k  
10   material (used to reduce inter- and intra-line capacitance and cross-talk)  
11   which typically suffers from poorer adhesion characteristics and lower  
12   thermal stability than traditional oxide insulators. Consequently, this places  
13   more stringent requirements on the barrier material and deposition method.  
14   An inferior adhesion layer will, for example, lead to delamination at either the  
15   barrier-to-dielectric or barrier-to-copper interfaces during any subsequent  
16   anneal and/or chemical mechanical planarization (CMP) processing steps  
17   leading to degradation in device performance and reliability. Ideally, the  
18   barrier layer should be thin, conformal, defect free, and of low resistivity so as  
19   to not compromise the conductance of the copper metal interconnect  
20   structure.

21        In addition, electroplating fill requires a copper seed layer, which  
22   serves to both carry the plating current and act as the nucleation layer. The  
23   preferred seed layer should be smooth, continuous, of high purity, and have  
24   good step coverage with low overhang. A discontinuity in the seed layer will

1 lead to sidewall voiding, while gross overhang will lead to pinch-off and the  
2 formation of top voids.

3 Both the barrier and seed layers which are critical to successful  
4 implementation of copper interconnects require a means of depositing high  
5 purity, conformal, ultra-thin films at low substrate temperatures.

6 Physical vapor deposition (PVD) or sputtering has been adopted as the  
7 preferred method of choice for depositing conductor films used in IC  
8 manufacturing. This choice has been primarily driven by the low cost, simple  
9 sputtering approach whereby relatively pure elemental or compound  
10 materials can be deposited at relatively low substrate temperatures. For  
11 example, refractory based metals and metal compounds such as tantalum  
12 (Ta), tantalum nitride (TaN<sub>x</sub>), other tantalum containing compounds, tungsten  
13 (W), tungsten nitride (WN<sub>x</sub>), and other tungsten containing compounds which  
14 are used as barrier/adhesion layers can be sputter deposited with the  
15 substrate at or near room temperature. However, as device geometries have  
16 decreased, the step coverage limitations of PVD have increasingly become an  
17 issue since it is inherently a line-of-sight process. This limits the total number  
18 of atoms or molecules which can be delivered into the patterned trench or via.  
19 As a result, PVD is unable to deposit thin continuous films of adequate  
20 thickness to coat the sides and bottoms of high aspect ratio trenches and vias.  
21 Moreover, medium/high-density plasma and ionized PVD sources developed  
22 to address the more aggressive device structures are still not adequate and are  
23 now of such complexity that cost and reliability have become serious  
24 concerns.

1       Chemical vapor deposition (CVD) processes offer improved step  
2    coverage since CVD processes can be tailored to provide conformal films.  
3    Conformality ensures the deposited films match the shape of the underlying  
4    substrate, and the film thickness inside the feature is uniform and equivalent  
5    to the thickness outside the feature. Unfortunately, CVD requires  
6    comparatively high deposition temperatures, suffers from high impurity  
7    concentrations, which impact film integrity, and have higher cost-of-  
8    ownership due to long nucleation times and poor precursor gas utilization  
9    efficiency. Following the tantalum containing barrier example, CVD Ta and  
10   TaN films require substrate temperatures ranging from 500 °C to over 800 °C  
11   and suffer from impurity concentrations (typically of carbon and oxygen)  
12   ranging from several to tens of atomic % concentration. This generally leads  
13   to high film resistivities (up to several orders of magnitude higher than PVD),  
14   and other degradation in film performance. These deposition temperatures  
15   and impurity concentrations make CVD Ta and TaN unusable for IC  
16   manufacturing, in particular for copper metallization and low-k integration.

17       Chen et al. ("Low temperature plasma-assisted chemical vapor  
18    deposition of tantalum nitride from tantalum pentabromide for copper  
19    metallization", J. Vac. Sci. Technol. B 17(1), pp. 182-185 (1999); and "Low  
20    temperature plasma-promoted chemical vapor deposition of tantalum from  
21    tantalum pentabromide for copper metallization", J. Vac. Sci. Technol. B 16(5),  
22    pp. 2887-2890 (1998)) have demonstrated a plasma-assisted (PACVD) or  
23    plasma-enhanced (PECVD) CVD approach using tantalum pentabromide  
24    ( $TaBr_5$ ) as the precursor gas to reduce the deposition temperature. Ta and

1     $\text{TaN}_x$  films were deposited from 350 °C to 450 °C and contained 2.5 to 3  
2    atomic % concentration of bromine. Although the deposition temperature has  
3    been reduced by increased fragmentation (and hence increased reactivity) of  
4    the precursor gases in the gas-phase via a plasma, the same fragmentation  
5    leads to the deposition of unwanted impurities. Gas-phase fragmentation of  
6    the precursor into both desired and undesired species inherently limits the  
7    efficacy of this approach.

8        Recently, atomic layer chemical vapor deposition (AL-CVD) or atomic  
9    layer deposition (ALD) has been proposed as an alternative method to CVD  
10   for depositing conformal, ultra-thin films at comparatively lower  
11   temperatures. ALD is similar to CVD except that the substrate is sequentially  
12   exposed to one reactant at a time. Conceptually, it is a simple process: a first  
13   reactant is introduced onto a heated substrate whereby it forms a monolayer  
14   on the surface of the substrate. Excess reactant is pumped out. Next a second  
15   reactant is introduced and reacts with the first reactant to form a monolayer of  
16   the desired film via a self-limiting surface reaction. The process is self-  
17   limiting since the deposition reaction halts once the initially adsorbed (physi-  
18   or chemi-sorbed) monolayer of the first reactant has fully reacted with the  
19   second reactant. Finally, the excess second reactant is evacuated. The above  
20   sequence of events comprises one deposition cycle. The desired film  
21   thickness is obtained by repeating the deposition cycle the required number  
22   of times.

23        In practice, ALD is complicated by the painstaking selection of a  
24   process temperature setpoint wherein both: 1) at least one of the reactants

1 sufficiently adsorbs to a monolayer and 2) the surface deposition reaction can  
2 occur with adequate growth rate and film purity. If the substrate temperature  
3 needed for the deposition reaction is too high, desorption or decomposition of  
4 the first adsorbed reactant occurs, thereby eliminating the layer-by-layer  
5 process. If the temperature is too low, the deposition reaction may be  
6 incomplete (i.e., very slow), not occur at all, or lead to poor film quality (e.g.,  
7 high resistivity and/or high impurity content). Since the ALD process is  
8 entirely thermal, selection of available precursors (i.e., reactants) that fit the  
9 temperature window becomes difficult and sometimes unattainable. Due to  
10 the above-mentioned temperature related problems, ALD has been typically  
11 limited to the deposition of semiconductors and insulators as opposed to  
12 metals. ALD of metals has been confined to the use of metal halide  
13 precursors. However, halides (e.g., Cl, F, Br) are corrosive and can create  
14 reliability issues in metal interconnects.

15 Continuing with the TaN example, ALD of TaN films is confined to a  
16 narrow temperature window of 400 °C to 500 °C, generally occurs with a  
17 maximum deposition rate of 0.2 Å/cycle, and can contain up to several  
18 atomic percent of impurities including chlorine and oxygen. Chlorine is a  
19 corrosive, can attack copper, and lead to reliability concerns. The above  
20 process is unsuitable for copper metallization and low-k integration due to  
21 the high deposition temperature, slow deposition rate, and chlorine impurity  
22 incorporation.

23 In conventional ALD of metal films, gaseous hydrogen (H<sub>2</sub>) or  
24 elemental zinc (Zn) is often cited as the second reactant. These reactants are

1 chosen since they act as a reducing agent to bring the metal atom contained in  
2 the first reactant to the desired oxidation state in order to deposit the end film.  
3 Gaseous, diatomic hydrogen (H<sub>2</sub>) is an inefficient reducing agent due to its  
4 chemical stability, and elemental zinc has low volatility (e.g., it is very  
5 difficult to deliver sufficient amounts of Zn vapor to the substrate) and is  
6 generally incompatible with IC manufacturing. Unfortunately, due to the  
7 temperature conflicts that plague the ALD method and lack of kinetically  
8 favorable second reactant, serious compromises in process performance  
9 result.

10 In order to address the limitations of traditional thermal or pyrolytic  
11 ALD, radical enhanced atomic layer deposition (REALD, US Patent 5,916,365)  
12 or plasma-enhanced atomic layer deposition has been proposed whereby a  
13 downstream radio-frequency (RF) glow discharge is used to dissociate the  
14 second reactant to form more reactive radical species which drives the  
15 reaction at lower substrate temperatures. Using such a technique, Ta ALD  
16 films have been deposited at 0.16 to 0.5 Å/cycle at 25 °C, and up to  
17 approximately 1.67 Å/cycle at 250 °C to 450 °C. Although REALD results in a  
18 lower operating substrate temperature than all the aforementioned  
19 techniques, the process still suffers from several significant drawbacks.  
20 Higher temperatures must still be used to generate appreciable deposition  
21 rates. Such temperatures are still too high for some films of significant  
22 interest in IC manufacturing such as polymer-based low-k dielectrics that are  
23 stable up to temperatures of only 200 °C or less. REALD remains a thermal or  
24 pyrolytic process similar to ALD and even CVD since the substrate

1 temperature provides the required activation energy for the process and is  
2 therefore the primary control means for driving the deposition reaction.

3 In addition, Ta films deposited using REALD still contain chlorine as  
4 well as oxygen impurities, and are of low density. A low density or porous  
5 film leads to a poor barrier against copper diffusion since copper atoms and  
6 ions have more pathways to traverse the barrier material. Moreover, a porous  
7 or under-dense film has lower chemical stability and can react undesirably  
8 with overlying or underlying films, or with exposure to gases commonly used  
9 in IC manufacturing processes.

10 Another limitation of REALD is that the radical generation and  
11 delivery is inefficient and undesirable. RF plasma generation of radicals used  
12 as the second reactant such as atomic H is not as efficient as microwave  
13 plasma due to the enhanced efficiency of microwave energy transfer to  
14 electrons used to sustain and dissociate reactants introduced in the plasma.

15 Furthermore, having a downstream configuration whereby the radical  
16 generating plasma is contained in a separate vessel located remotely from the  
17 main chamber where the substrate is situated and using a small aperture to  
18 introduce the radicals from the remote plasma vessel to the main chamber  
19 body significantly decreases the efficiency of transport of the second radical  
20 reactant. Both gas-phase and wall recombination will reduce the flux of  
21 desired radicals that can reach the substrate. In the case of atomic H, these  
22 recombination pathways will lead to the formation of diatomic H<sub>2</sub>, a far less  
23 effective reducing agent. If the plasma used to generate the radicals was

1 placed directly over the substrate, then the deposition of unwanted impurities  
2 and particles can occur similarly to the case of plasma-assisted CVD.

3 Finally, ALD (or any derivative such as REALD) is fundamentally slow  
4 since it relies on a sequential process whereby each deposition cycle is  
5 comprised of at least two separate reactant flow and evacuation steps, which  
6 can occur on the order of minutes with conventional valve and chamber  
7 technology. Significant improvements resulting in faster ALD are needed to  
8 make it more suitable for commercial IC manufacturing.

1    **Brief Description of The Drawings**

2        Figure 1 is a schematic of a deposition system suitable for modulated  
3        ion-induced atomic layer deposition (MII-ALD).

4        Figure 2A depicts a timing sequence for an improved ALD method  
5        incorporating periodic exposure of the substrate to ions.

6        Figure 2B is another timing sequence for an improved ALD method  
7        incorporating periodic exposure of the substrate to ions.

8        Figure 3A shows the MII-ALD method utilizing ion flux modulation to  
9        vary the substrate exposure to ions.

10       Figure 3B shows the timing of the MII-ALD method utilizing ion  
11       energy modulation to vary the substrate exposure to ions by varying the  
12       substrate bias.

13       Figures 4A-F show methods of modulating the MII-ALD process.

14       Figure 5 shows an electrostatic chuck (ESC) system suitable for  
15       modulating the ion energy in the MII-ALD process: a) in topological form;  
16       and, b) as an equivalent electrical circuit.

17

1    **Summary and Detailed Description of the Invention**

2       The present invention relates to methods and apparatuses useable for  
3       the deposition of conformal solid thin films of one or more elements at low  
4       temperature. More particularly, the present invention relates to an enhanced  
5       sequential or, more preferably, non-sequential atomic layer deposition  
6       apparatus and technique suitable for deposition of barrier layers, adhesion  
7       layers, seed layers, and low dielectric constant (low-k) films, high dielectric  
8       constant (high-k) films, and other conductive, semi-conductive, and non-  
9       conductive thin films.

10      More specifically, the present invention resolves the previously  
11     presented problems encountered in the prior art (e.g., REALD) by 1)  
12     providing a non-thermal or non-pyrolytic means of triggering the deposition  
13     reaction; 2) providing a means of depositing a purer film of higher density at  
14     lower temperatures; 3) providing a faster and more efficient means of  
15     modulating the deposition sequence and hence the overall process rate  
16     resulting in an improved deposition method; and, 4) providing a means of  
17     improved radical generation and delivery.

18      Improvements to ALD processing, e.g., the REALD mentioned  
19     previously, remain "thermal" or "pyrolytic" processes since the substrate  
20     temperature provides the required activation energy and is the primary  
21     control knob for driving the deposition reaction. Alternatively, we propose a  
22     novel approach by providing the required activation energy from a "non-  
23     thermal" source. In particular, we propose driving the deposition reaction  
24     primarily via substrate exposure to impinging ions wherein the ions are used

- 1 to deliver the necessary activation energy to the near surface atoms and
- 2 adsorbed reactant(s) via collision cascades.

3           Conventional deposition processes used in the semiconductor industry  
4 (including ALD) typically deposit materials at temperatures in the range of  
5 300-600 °C. The deposition method described herein can be effected at much  
6 lower temperatures, in practice as low as 25 °C or below. Note that this  
7 process is ion-triggered (i.e., ion-induced) as opposed to ion-assisted in that  
8 deposition will not generally occur without ion bombardment since ions are  
9 used as the primary means of providing the activation energy required for  
10 deposition. A primary benefit of ion-induced processing is the deposition of  
11 higher density films of superior purity and adhesion properties. This result  
12 occurs due to ion bombardment induced densification.

13           Figure 1 illustrates a deposition system suitable for modulated ion-  
14 induced atomic layer deposition (MII-ALD). The invention described herein  
15 also incorporates a means of modulating the exposure of the substrate to ions.  
16 By modulating 1) the ion flux; 2) the energy of the ions striking the substrate;  
17 or a combination of (1) and (2), the deposition reaction can be precisely  
18 toggled "on" or "off". If the ion flux or energy is at a "low" state, then no  
19 deposition results or deposition occurs so slowly that essentially no  
20 deposition results. If the impinging ion flux or energy is at a "high" state,  
21 then deposition occurs. Since the substrate (which may be a "bare" substrate,  
22 e.g., a silicon wafer before any films have been deposited, or it may be a  
23 substrate which may already have had one or more films deposited on its  
24 surface) 181 is preferably maintained at a low substrate temperature, the first

1 and second reactants do not thermally react with any appreciable rate or do  
2 not react at all. Instead, the deposition reaction only takes place when either  
3 the ion flux or ion energy is toggled to a suitable "high state". The desired  
4 film thickness is built up by repeating the ion pulses (either of flux or energy)  
5 the required number of cycles. Furthermore, since modulation of the ion flux  
6 or ion energy can occur on a much faster time scale (KHz range) than the  
7 conventional valve and pump technology used in ALD (up to minutes per  
8 cycle), this deposition method is more suitable for commercial IC  
9 manufacturing. This method shall be referred to herein as modulated ion-  
10 induced atomic layer deposition (MII-ALD).

11 In addition, the present invention also improves upon the prior art by  
12 employing a microwave generated plasma 172 substantially contained in the  
13 main chamber body 190 that is isolated via a distribution showerhead 171  
14 comprised of a series or array of apertures 175 which resolves the issues of  
15 radical generation and delivery, while preventing gas-phase precursor  
16 cracking (i.e., fragmentation or breaking down the precursor gas into its  
17 constituent elements) and impurity and/or particle generation directly above  
18 the wafer 181. The plasma is contained within the plasma source chamber 170  
19 itself and is not in direct communication with the substrate 181. In MII-ALD,  
20 the same plasma is used to generate both ions 177 (used to drive the surface  
21 reactions) and radicals 176 (used as the second reactant), but is isolated from  
22 the first reactant 100 which typically contains both the principal element(s)  
23 desired in the end film, but also unwanted impurity containing byproducts.  
24 Therefore, primarily only the radicals 176 and ions 177 are able to travel

1 through the showerhead apertures 175. The plasma 172 is essentially  
2 contained within the plasma source chamber and does not intermingle with  
3 the precursor gases 100, 120.

4 The present invention utilizes ion imparted kinetic energy transfer  
5 rather than thermal energy (e.g., REALD, ALD, PECVD, CVD, etc.) to drive  
6 the deposition reaction. Since temperature can be used as a secondary control  
7 variable, with this enhancement films can be deposited using MII-ALD at  
8 arbitrarily low substrate temperatures (generally less than 350 °C). In  
9 particular, films can be deposited at or near room temperature (i.e., 25°C) or  
10 below.

11 The system of Figure 1 contains a substantially enclosed plasma source  
12 chamber 170 located in substantial communication with or, more preferably,  
13 substantially within a main chamber body 190. The plasma 172 is used to  
14 dissociate feed gases 130, 110 to generate both ions 177 and radicals 176.  
15 Typical feed gases 130 used for ion generation include, but are not restricted  
16 to Ar, Kr, Ne, and Xe. Typical feed gases 110 (e.g., precursor B) used for  
17 radical generation include, but are not restricted to H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O  
18 vapor. The ions 177 are used to deliver the energy needed to drive surface  
19 reactions between the first adsorbed reactant and the generated radicals 176.  
20 Inductively coupled RF (e.g., 400 KHz, 2 MHz, 13.56 MHz, etc.) power 160 can  
21 be used to generate the plasma via solenoidal coils located within or outside  
22 of the plasma chamber (not shown in Figure 1). More preferably, microwave  
23 (e.g., generally 2.45 GHz or higher frequencies) power 160 is coupled to the  
24 plasma source chamber 170 via a suitable means such as a waveguide or

1 coaxial cable. Microwave energy can be more efficiently transferred to  
2 ionizing electrons, leading to higher ionization fractions. This is of particular  
3 importance in the generation of radicals 176 (i.e., a chemical fragment of a  
4 larger molecule) such as atomic hydrogen, or any of a number of other  
5 reactive groups such as nitrogen atoms (N), oxygen atoms (O), OH molecules,  
6 or NH molecules, or a combination thereof. These radicals serve as the  
7 second reactant. Microwave or radio-frequency (RF) power 160 is coupled to  
8 the plasma 172 via a dielectric material 173, which may be a dielectric window  
9 such as quartz embedded in the chamber wall, or it may be empty space in  
10 the case of a microwave or RF antenna located within the plasma chamber.

11 In addition, a distribution showerhead 171, containing a series or array  
12 of apertures 175 through which ions 177 and radicals 176 are delivered to the  
13 substrate 181, isolates the main process chamber 180 from the plasma source  
14 chamber 170. A pressure drop (for example, a 5 or 10 times decrease in  
15 pressure, with the main processing chamber 180 being at the lower pressure)  
16 is thereby created between the plasma source chamber 170 and the main  
17 processing chamber 180 to project the ions 177 and radicals 176 to the  
18 substrate 181 via the distribution showerhead 171. The plasma source  
19 chamber 170 is generally of comparable diameter to the main chamber body  
20 190 to enable large area exposure of the sample. The size, aspect ratio, and  
21 distribution of the showerhead apertures 175 can be optimized to provide  
22 uniform exposure of the substrate 181 and the desired ion 177 to radical 176  
23 ratio. The distance between this showerhead 171 and the substrate 181 may  
24 vary depending on the application. For the processing of wafers in the IC

1 industry, this distance is preferably at most two wafer diameters and more  
2 preferably less than or equal to one half a wafer diameter.

3 Having a substantially enclosed plasma generation chamber 170  
4 situated within the main chamber 190 allows efficient and uniform delivery of  
5 ions 177 and radicals 176 to the substrate 181. In addition, by isolating the  
6 plasma 172 from the main chamber 180 prevents gas-phase cracking of the  
7 first reactant 100 (e.g., precursor A), which is introduced directly to the main  
8 processing chamber 180 via a gas distribution manifold 199. Precursor A 100  
9 may be any one or more of a series of gaseous compounds used for depositing  
10 semiconductors, insulators, metals or the like that are well-known in the art  
11 (e.g., PDEAT (pentakis(diethylamido)tantalum), PEMAT  
12 (pentakis(ethylmethylamido)tantalum), TaBr<sub>5</sub>, TaCl<sub>5</sub>, TBTDET (t-butylimino  
13 tris(diethylamino) tantalum), TiCl<sub>4</sub>, TDMAT  
14 (tetrakis(dimethylamido)titanium), TDEAT (tetrakis(diethylamino)titanium),  
15 CuCl, Cupraselect<sup>®</sup> ((Trimethylvinylsilyl)hexafluoroacetylacetonato Copper  
16 I), W(CO)<sub>6</sub>, WF<sub>6</sub>, etc.) and examples will be further discussed herein. Finally,  
17 the ion/radical distribution showerhead 171 shields the dielectric wall 173  
18 adjacent to the supplied RF or microwave power 160 against being coated by  
19 precursor A 100 during processing which can degrade power transfer to the  
20 plasma 172 in processing systems found in the prior art. This is of particular  
21 importance in the case of deposition of conductors whereby if the dielectric  
22 173 is fully exposed to the metal containing first reactant 100 (e.g., precursor  
23 A) and if the plasma 172 was directly generated within the main chamber 190  
24 without the use of an isolating distribution showerhead 171, then metal

1 deposition onto the dielectric 173 will eventually shield out RF or microwave  
2 power 160 from the plasma 172 such that the plasma 172 will extinguish.

3 Figure 2A depicts a sequence for an improved ALD method  
4 incorporating periodic exposure of the substrate to ions. In this variant of the  
5 method, ion exposure 230 begins with the introduction of the second  
6 precursor 220 (especially when plasma generated radicals 176 are used as the  
7 second precursor or reactant). This figure illustrates one embodiment of MII-  
8 ALD utilizing the apparatus described in Figure 1. This results in an  
9 enhanced sequential ALD process as follows:

10 1) First exposure 200: The substrate 181 is exposed to a first gaseous  
11 reactant 100 (e.g., precursor A), allowing a monolayer of the reactant to form  
12 on the surface. The substrate 181 may be at any temperature below the  
13 decomposition temperature of the first gaseous reactant although it is  
14 preferable for the temperature to generally be less than approximately 350 °C.

15 2) First evacuation 210: The excess reactant 100 is removed by  
16 evacuating 214 the chamber 180 with a vacuum pump 184.

17 3) Second exposure 220: Unlike conventional ALD, the substrate 181 is  
18 simultaneously exposed to ions 177 and a second gaseous reactant (e.g.,  
19 microwave or RF plasma generated radicals 176) during this step with the  
20 substrate 181 (e.g., wafer) biased to a negative potential  $V_{bias}$  185. Microwave  
21 or RF power 160 is supplied into the plasma chamber 170 to generate both the  
22 ions 177 (e.g., argon-ion ( $Ar^+$ )) and radicals 176 (e.g., H atoms). The ions will  
23 strike the wafer 181 with an energy approximately equal to  $(e|V_{bias}| + e|V_p|)$   
24 where  $V_p$  is the plasma 172 potential (typically 10V to 20V).  $V_{bias}$  (-20V to -

1 500V) is typically chosen to be greater than  $V_p$  in magnitude, and is used to  
2 control the ion 177 energy. With the activation energy now primarily  
3 supplied by ions 177 instead of thermal energy, the first and second (chemi-  
4 or physi-sorbed) reactants react via an ion-induced surface reaction to  
5 produce a solid thin monolayer of the desired film at a reduced substrate  
6 temperature below conventional ALD. The deposition reaction between the  
7 first and second reactants is self-limiting in that the reaction between them  
8 terminates after the initial monolayer of the first reactant 100 is consumed.

9 4) Second evacuation 210: The excess second reactant is removed by  
10 again evacuating 216 the chamber 180 with the vacuum pump 184.

11 5) Repeat: The desired film thickness is built up by repeating the entire  
12 process cycle (steps 1-4) many times.

13 Additional precursor gases (e.g., 120, 140) may be introduced and  
14 evacuated as required for a given process to create tailored films of varying  
15 compositions or materials. As an example, an optional exposure may occur in  
16 the case of a compound barrier of varying composition. For example, a  
17  $TaN_x/Ta$  film stack is of interest in copper technology since  $TaN_x$  prevents  
18 fluorine attack from the underlying fluorinated low-k dielectrics, whereas the  
19 Ta promotes better adhesion and crystallographic orientation for the  
20 overlying copper seed layer. The  $TaN_x$  film may be deposited using a  
21 tantalum containing precursor (e.g.,  $TaCl_5$ , PEMAT, PDEAT, TBTDET) as the  
22 first reactant 100 (precursor A) and a mixture of atomic hydrogen and atomic  
23 nitrogen (i.e. flowing a mixture of  $H_2$  and  $N_2$  into the plasma source 172) as  
24 the second reactant to produce a  $TaN_x$  film. Simultaneous ion exposure is

1 used to drive the deposition reaction. Next a Ta film may be deposited in a  
2 similar fashion by using atomic hydrogen (as opposed to a mixture of atomic  
3 hydrogen and nitrogen) as the second reactant. An example of a tailored film  
4 stack of differing materials can be the subsequent deposition of a copper layer  
5 over the  $TaN_x/Ta$  bi-layer via the use of a copper containing organometallic  
6 (e.g.,  $Cu(TMVS)(hfac)$  or (Trimethylvinylsilyl)hexafluoroacetylacetoneato  
7 Copper I, also known by the trade name CupraSelect<sup>®</sup>, available from  
8 Schumacher, a unit of Air Products and Chemicals, Inc., 1969 Palomar Oaks  
9 Way, Carlsbad, CA 92009 ) or inorganic precursor (e.g.  $CuCl$ ) shown as  
10 precursor C 120 in Figure 1. The copper layer can serve as the seed layer for  
11 subsequent electroless or electroplating deposition.

12 A variant of the method shown in Figure 2A is illustrated in Figure 2B  
13 where ion exposure is initiated after the second reactant exposure. Figure 2B  
14 depicts a sequence for an improved ALD method incorporating periodic  
15 exposure of the substrate 181 to ions 177. In this variant of the method, ion  
16 exposure 280 begins with the evacuation 250 of the second precursor 256  
17 (especially when the second precursor or reactant is not subjected to a  
18 plasma). Typically, this is the case where the second precursor or reactant is  
19 not a plasma-generated radical.

20 In the previous embodiments of MII-ALD, although the deposition  
21 temperature can be lowered significantly, the first and second reactants are  
22 still sequentially introduced into the main process chamber 180, and hence  
23 will still be a slow process. It is of particular interest to eliminate or replace

1 the time-consuming flow-evacuation-flow-evacuation sequential nature of the  
2 process.

3 In the preferred embodiment of the MII-ALD process, a substrate 181  
4 heated (e.g., to a low temperature of less than or equal to 350 °C) or unheated  
5 is simultaneously exposed to a first reactant and a second reactant, and  
6 subjected to modulated ion 177 exposure. By modulating 1) the ion flux (i.e.  
7 the number of ions hitting the substrate per unit area per unit time); 2) the  
8 energy of the ions striking the substrate; or a combination of (1) and (2), the  
9 deposition reaction can be precisely toggled "on" or "off". Since the substrate  
10 181 is preferably maintained at a low substrate temperature, the first and  
11 second reactants do not thermally react with any appreciable rate or do not  
12 react at all when the ion flux or energy is toggled to a "low" state. Instead,  
13 the deposition reaction only takes place when either the ion flux or ion energy  
14 is toggled to a suitable "high state". Ion flux or energy modulation can vary  
15 generally from 0.1 Hz to 20 MHz, preferably from 0.01 KHz to 10 KHz.  
16 During deposition, the main process chamber 180 pressure can be maintained  
17 in the range of generally  $10^2$  to  $10^7$  torr, more preferably from  $10^1$  to  $10^4$  torr,  
18 depending on the chemistry involved. The desired film thickness is attained  
19 via exposure of the substrate to the suitable number of modulated ion flux or  
20 energy pulse cycles. This MII-ALD scheme results in a "continuous"  
21 deposition process that is significantly faster than conventional sequential  
22 ALD since the two, slow evacuation steps (up to minutes) are eliminated and  
23 replaced by the faster (KHz range or above) ion modulation steps. The

1 modulation can be either of the ion flux via the plasma power or of the ion  
2 energy via an applied periodic wafer bias.

3 The MII-ALD method utilizing ion flux modulation to control the  
4 deposition cycle is illustrated conceptually in Figure 3A, with the flux  
5 modulation scheme described more explicitly in Figures 4A and 4C. Figure  
6 3A depicts the MII-ALD method utilizing ion flux modulation 320 to vary the  
7 substrate 181 exposure to ions 177. Note that the second reactant 310, e.g.,  
8 radicals, is synchronized with the ion flux via 320 plasma power modulation,  
9 causing a periodic exposure of the substrate to ions and radicals. Varying the  
10 power 160 delivered to the plasma 172 can vary the ion flux from little or  
11 none to maximum ion production. Plasma power modulation can take the  
12 form of variations in frequency (periodicity), magnitude, and duty-cycle.

13 Increasing plasma power 160 leads to increasing plasma 172, and hence,  
14 increased ion 177 density. Since the deposition process is ion-induced, having  
15 little or no ion bombardment will essentially stop the deposition process,  
16 whereas increased ion bombardment will cause deposition to occur. A  
17 constant wafer bias 185 (DC in Figure 4C or RF in Figure 4A) is applied to  
18 define the ion energy of the modulated ion flux in this embodiment and is  
19 chosen to be sufficiently high so that ion-induced surface reactions can occur.

20 Note that in this embodiment since the plasma (either RF or preferably  
21 microwave) power 160 is used to generate both ions 177 and radicals 176, the  
22 second reactant (e.g., radicals) flux 310 is synchronized with the ion flux 320  
23 pulses. The radical feed gas 110 ( $H_2$ , for example) flow, however, does not

1 change. Instead, the radical flux 310 (e.g., fraction of H<sub>2</sub> which is converted to  
2 atomic H) is modulated.

3 Alternatively, subjecting the substrate 181 to a non-constant wafer  
4 voltage bias 185 can vary the incoming ion energy at a fixed plasma power  
5 160 (i.e., ion flux). This preferred embodiment of MII-ALD is illustrated  
6 conceptually in Figures 3B, and more explicitly in Figures 4B and 4D. Figure  
7 3B shows the MII-ALD method utilizing ion energy modulation 350 to vary  
8 the substrate 181 exposure to ions 177 by varying the substrate bias 185. The  
9 applied bias 185 can take the form of variations in frequency (periodicity),  
10 magnitude, and duty-cycle. A DC as shown in Figure 4D or RF (e.g., 400  
11 kHz, 2 MHz, 13.56 MHz, etc.) as shown in Figure 4B power supply can be  
12 used. When the wafer potential is "low" (e.g., near or at zero with respect to  
13 ground), the incoming ions 177 do not have enough energy to induce surface  
14 deposition reactions. When the wafer 181 potential is "high" (e.g., at a  
15 significant negative potential relative to ground), the incoming ions 177 will  
16 have the necessary energy to induce surface deposition reactions via collision  
17 cascades. In such a fashion, the deposition can be turned "on" or "off" by  
18 modulating the wafer bias voltage 185, and hence the impinging ion 177  
19 energy. Typical wafer voltages can range from generally -20 V to -1000 V,  
20 but preferably in the -25 V to -500 V range, and more preferably in the -50 V  
21 to -350 V range during deposition. The bias voltage 185 is coupled to the  
22 wafer via the pedestal 182. Preferably, the substrate pedestal 182 is an  
23 electrostatic chuck (ESC) to provide efficient coupling of bias voltage to the  
24 substrate. The ESC is situated in the main processing chamber 180 and can be

1    cooled via a fluid coolant (preferably a liquid coolant) and/or heated (e.g.,  
2    resistively) to manipulate the substrate temperature.

3        As illustrated in Figure 5 for the case of an applied DC bias, the  
4    preferred electrostatic chuck is a "coulombic" ESC 500 (bulk resistivity  
5    generally greater than  $10^{13}$  ohm-cm) rather than one whose bulk material  
6    effects are dominated by the Johnson-Rahbek (JR) effect (bulk resistivity  
7    between  $10^8$  and  $10^{12}$  ohm-cm). Typically, the substrate potential is a complex  
8    function of the voltage of the electrostatic "chucking" electrodes if these  
9    voltages are established relative to a reference potential, but is simplified in  
10   the case of "coulombic" (non-JR) ESC. However, if the power supply 510 that  
11   powers the ESC 500 is truly floating, i.e., the entire system has a high  
12   impedance to the chamber 180 potential (usually ground) including the  
13   means of supplying power, then the substrate potential can be arbitrary. In  
14   particular, if the ESC power supply 510 is also center-tapped 518, then the  
15   wafer potential can be established by connecting the center tap 518 to the  
16   output of a power amplifier 520. This power amplifier can be controlled by a  
17   computer or a waveform generator 530 to periodically drop the substrate  
18   potential to a negative value for a certain period of time. It is desired to have  
19   independent control of the magnitude, frequency (periodicity), and duty cycle  
20   of this substrate bias pulse train. Such an ESC system is depicted in Figure 5,  
21   which shows an ESC system suitable for modulating the ion energy in the  
22   MII-ALD process: a) in topological form; and, b) as an equivalent electrical  
23   circuit.

1        The deposition rate is affected by the choice of the critical bias pulse  
2    train variables: the magnitude, frequency (periodicity), and duty cycle.  
3    Preferably, when the bias frequency is high (e.g., 100 Hz-10 KHz) with a short  
4    duty cycle (e.g., less than 30%), reducing the net, time-averaged current  
5    (which can cause substrate potential drift, de-chucking problems, or charge-  
6    induced device damage) while providing a charge relaxation period wherein  
7    the ion charges accumulated during ion exposure can redistribute and  
8    neutralize.

9        Once the deposition rate is calibrated for a particular recipe  
10   (Angstroms/cycle), the ability to accurately determine the film thickness by  
11   counting cycles is a further benefit of this modulation scheme. The higher the  
12   frequency, the finer the resolution of this critical deposition process  
13   performance metric.

14        Alternatively, the substrate potential can be modulated by imparting  
15   an induced DC bias to the substrate by applying RF power to the pedestal.  
16   Preferably, the RF power is coupled into the ESC electrodes. Figures 4A-F  
17   illustrate the preferred methods of modulating the MII-ALD process. In  
18   Figure 4A, an RF bias power  $B_2$  is applied to the substrate pedestal 182  
19   imparting an induced DC bias  $V_2$  to the substrate while the plasma (either  
20   microwave or RF) power 400 is varied periodically between a high  $P_1$  and a  
21   low  $P_2$  power state. In Figure 4B, plasma (either microwave or RF) power 410  
22   is constant  $P_1$  while an RF bias power, applied to the substrate pedestal 182, is  
23   varied between a low  $B_1$  and a high  $B_2$  bias state ( $V_1$  and  $V_2$  are the DC offset or  
24   bias voltages resulting from the applied RF bias power). In Figure 4C, a

1 negative DC bias 425 is applied to the substrate pedestal 182 while the plasma  
2 (either microwave or RF) power 420 is varied periodically between a high  $P_1$ ,  
3 and a low power  $P_2$  state. In Figure 4D, plasma (either microwave or RF)  
4 power is constant 430 while a DC bias 435 applied to the substrate pedestal  
5 182 is varied between a zero  $V_1$  and a negative voltage state  $V_2$ . In Figure 4E,  
6 a mechanical shutter periodically occludes the ion source. All the while, the  
7 plasma power 440 (either microwave or RF) and substrate voltage 445 are  
8 held constant. In Figure 4F, a source area that is smaller than the substrate  
9 181 is preferably used. In this case, plasma (either microwave or RF) power  
10 450 is constant, a negative DC substrate bias 455 is constant, and the source  
11 and substrate 181 are moved relative to each other 457, exposing only a  
12 portion of the substrate 181 at a time. The methods proposed in Figure 4B  
13 and Figure 4D, whereby the substrate bias is modulated at a constant plasma  
14 power 410, 430 and hence ion flux, are most preferred.

15 MII-ALD can be used to deposit dielectric, semiconducting, or metal  
16 films, among others, used in the semiconductor, data storage, flat panel  
17 display, and allied as well as other industries. In particular, the method and  
18 apparatus is suitable for the deposition of barrier layers, adhesion layers, seed  
19 layers, low dielectric constant (low-k) films, and high dielectric constant  
20 (high-k) films.

21 This process utilizes independent control over the three constituents of  
22 plasma – ions, atoms, and precursors. Decoupling these constituents offer  
23 improved control over the deposition process.

1        An added benefit of using MII-ALD is that with proper choice of the  
2    second reactant, selective ion-enhanced etching and removal of unwanted  
3    impurities can be performed. As an example, for many chemistries, the  
4    preferred second reactant is monatomic hydrogen (H) 176. Simultaneous  
5    energetic ion and reactive atomic H bombardment will cause selective  
6    removal of unwanted impurities (e.g., containing carbon, oxygen, fluorine, or  
7    chlorine) commonly associated with organometallic precursors (e.g., TBTDET,  
8    PEMAT, PDEAT, TDMAT, TDEAT), and proceed with removal rates superior  
9    to either chemical reaction (e.g., atomic H only) or physical sputtering (e.g.,  
10   Ar ion only) alone. Impurities lead to high film resistivities, low film density,  
11   poor adhesion, and other deleterious film effects. Alternatively, in addition to  
12   atomic hydrogen, other reactive groups such as nitrogen atoms (N), oxygen  
13   atoms (O), OH molecules, or NH molecules, or a combination thereof may be  
14   employed.

15        From the description of the preferred embodiments of the process and  
16   apparatus set forth above, it is apparent to one of ordinary skill in the art that  
17   variations and additions to the embodiments can be made without departing  
18   from the principles of the present invention. As an example, chlorine,  
19   bromine, fluorine, oxygen, nitrogen, hydrogen, other reactants and/or  
20   radicals containing the aforementioned elements or a combination thereof, in  
21   conjunction with energetic ion bombardment, can be used to effect etching or  
22   material removal as opposed to deposition. This is of particular importance  
23   in the cleaning of native oxides of copper, aluminum, silicon, and other  
24   common conductor and semiconductor materials used in IC manufacturing.

- 1 Either the deposition or etching can be accomplished globally (as illustrated
- 2 in the preceding embodiments) or may be chosen to be local to a controlled
- 3 area (i.e., site-specific using a small, ion beam point or broad-beam source
- 4 scanned or otherwise stepped across the substrate, exposing only a fraction of
- 5 the substrate area at any given time).

**System and Method for Modulated Ion-induced Atomic Layer Deposition  
(MII-ALD)**

**Claims**

**What is claimed is:**

1        1.    A sequential method for depositing a thin film onto a substrate  
2    in an evacuated chamber comprising:  
3        introducing a first reactant gas into said chamber;  
4        adsorption of at least one monolayer of said first reactant gas onto said  
5    substrate;  
6        evacuation of excess said first reactant gas from said chamber  
7        introduction of at least one ion generating feed gas into said chamber;  
8        generating a plasma from said ion generating feed gas to form ions;  
9        exposing said substrate to said ions;  
10      modulating said ions; and  
11      reacting said adsorbed monolayer of said first reactant gas with said  
12    ions to deposit said thin film.

1        2.    The method of claim 1, wherein said ion modulation is  
2    modulated in a way selected from the group consisting of modulating an ion  
3    flux and modulating an ion energy.

1        3.    The method of claim 1, further comprising maintaining said  
2    substrate at a temperature of between about 25 °C to 350 °C.

1           4.       A system for ion-induced atomic layer deposition of a film onto  
2       a substrate, said system comprising:  
3           a main chamber containing a plasma generation chamber for  
4       generating a plasma;  
5           said main chamber also containing a deposition chamber for  
6       depositing said film on said substrate;  
7           a distribution showerhead located between said plasma generation  
8       chamber and said deposition chamber;  
9           said plasma generation chamber coupled to receive at least one feed  
10      gas to form said plasma for generation of ions;  
11       said plasma generation chamber also coupled to receive at least one  
12      feed gas to react with said plasma for generation of radicals; and  
13       said deposition chamber coupled to receive at least one precursor gas  
14      to react with said ions and said radicals to form said film on said substrate.

1           5.       The system of claim 4, wherein said plasma generation chamber  
2       is in communication with a radio frequency energy source through a  
3       dielectric window.

1           6.       The system of claim 5, wherein said distribution showerhead  
2       shields said dielectric window from being coated by said deposition chamber  
3       precursor gas.

1        7.     The system of claim 4, wherein said plasma generation chamber  
2     is in communication with a microwave frequency energy source.

1        8.     The system of claim 4 further comprising a substrate holder  
2     located in said deposition chamber, said substrate holder electrically biasing  
3     said substrate via a power supply.

1        9.     The system of claim 8, wherein said power supply supplies a  
2     radio frequency power to induce said electrical bias on said substrate.

1        10.    The system of claim 4, wherein said plasma generated in said  
2     plasma generation chamber does not intermingle with said deposition  
3     chamber precursor gas.

1        11.    The system of claim 4, wherein said distribution showerhead is  
2     comprised of one or more apertures.

1        12.    The system of claim 4, wherein a deposition reaction is  
2     controlled via ion-imparted kinetic energy.

1        13.    The system of claim 4, further comprising a thermal heating  
2     element to control said film deposition on said substrate.

1           14.    A system for generating a plasma for depositing a film onto a  
2   substrate, said system comprising:  
3           a plasma generation source;  
4           a plasma generation chamber coupled to said plasma generation  
5   source;  
6           a deposition chamber; and  
7           a distribution showerhead separating said plasma generation chamber  
8   from said deposition chamber.

1           15.    The system of claim 14, wherein said plasma generation source  
2   may be modulated by a change selected from a group consisting of a change  
3   in frequency, a change in power magnitude, and a change in duty-cycle.

1        16.    A sequential method for depositing a thin film onto a substrate  
2    in an evacuated chamber comprising:  
3        introducing a first reactant gas into said chamber;  
4        adsorption of at least one monolayer of said first reactant gas onto said  
5    substrate;  
6        evacuation of excess said first reactant gas from said chamber  
7        introduction of at least one ion generating feed gas into said chamber;  
8        introduction of at least one radical generating feed gas into said  
9    chamber;  
10       generating a plasma from said ion generating feed gas and said radical  
11    generating feed gas to form ions and radicals;  
12       exposing said substrate to said ions and said radicals;  
13       modulating said ions; and  
14       reacting said adsorbed monolayer of said first reactant gas with said  
15    ions and said radicals to deposit said thin film.

1        17.    The method of claim 16, wherein said method is repeated until  
2    the film achieves a desired thickness.

1        18.    The method of claim 16, further comprising exposing said  
2    substrate to at least one additional reactant gas.

1        19.    The method of claim 16, wherein said substrate is  
2    simultaneously exposed to said ions and said radicals

1           20.    The method of claim 16, wherein said ion modulation is  
2   modulated in a way selected from the group consisting of modulating an ion  
3   flux and modulating an ion energy.

1           21.    The method of claim 20, wherein modulation in said ion flux is  
2   modulated in a way selected from the group consisting of modulating a flow  
3   of said ion generating feed gas, modulating a power of said plasma,  
4   modulating said exposure to said ions, and modulating the relative  
5   movement between said plasma and said substrate.

1           22.    The method of claim 16, further comprising maintaining said  
2   substrate at a temperature of between about 25 °C to 350 °C.

1           23.    The method of claim 16, further comprising inducing an  
2   electrical bias on said substrate via a substrate pedestal on which said  
3   substrate rests.

1           24.    The method of claim 23, wherein said pedestal is an electrostatic  
2   chuck (ESC) to provide coupling of said electrical bias to said substrate.

1           25.    The method of claim 23, wherein said electrical bias is induced  
2   by a radio frequency power supply.

1            26.    The method of claim 16, wherein an energy to generate said  
2    plasma is produced by a radio frequency source.

1            27.    The method of claim 16, wherein an energy to generate said  
2    plasma is produced by a microwave source.

1           28.    A method for depositing a thin film onto a substrate in an  
2    evacuated chamber comprising:  
3            placing said substrate onto a substrate holder in a deposition chamber  
4    area;  
5            introducing at least one ion generating feed gas into a plasma  
6    generation chamber area in communication with said deposition chamber  
7    area, but substantially isolated via a distribution showerhead comprised of  
8    one or more apertures located between said plasma generation chamber area  
9    and said deposition chamber area;  
10          introducing at least one radical generating feed gas into said plasma  
11    generation chamber area;  
12          generating a plasma from said ion generating feed gas to form ions;  
13          generating a plasma from said radical generating feed gas to form  
14    radicals;  
15          electrically biasing said substrate to a negative potential;  
16          introducing at least one reactant gas into said deposition chamber area;  
17          adsorbing at least one monolayer of said reactant gas on said substrate;  
18          exposing said substrate to said ions and said radicals;  
19          modulating said ions; and  
20          reacting said adsorbed monolayer of said reactant gas with said ions  
21    and said radicals to deposit said thin film.

1           29.    The method of claim 28, further comprising exposing said  
2    substrate to at least one additional reactant gas.

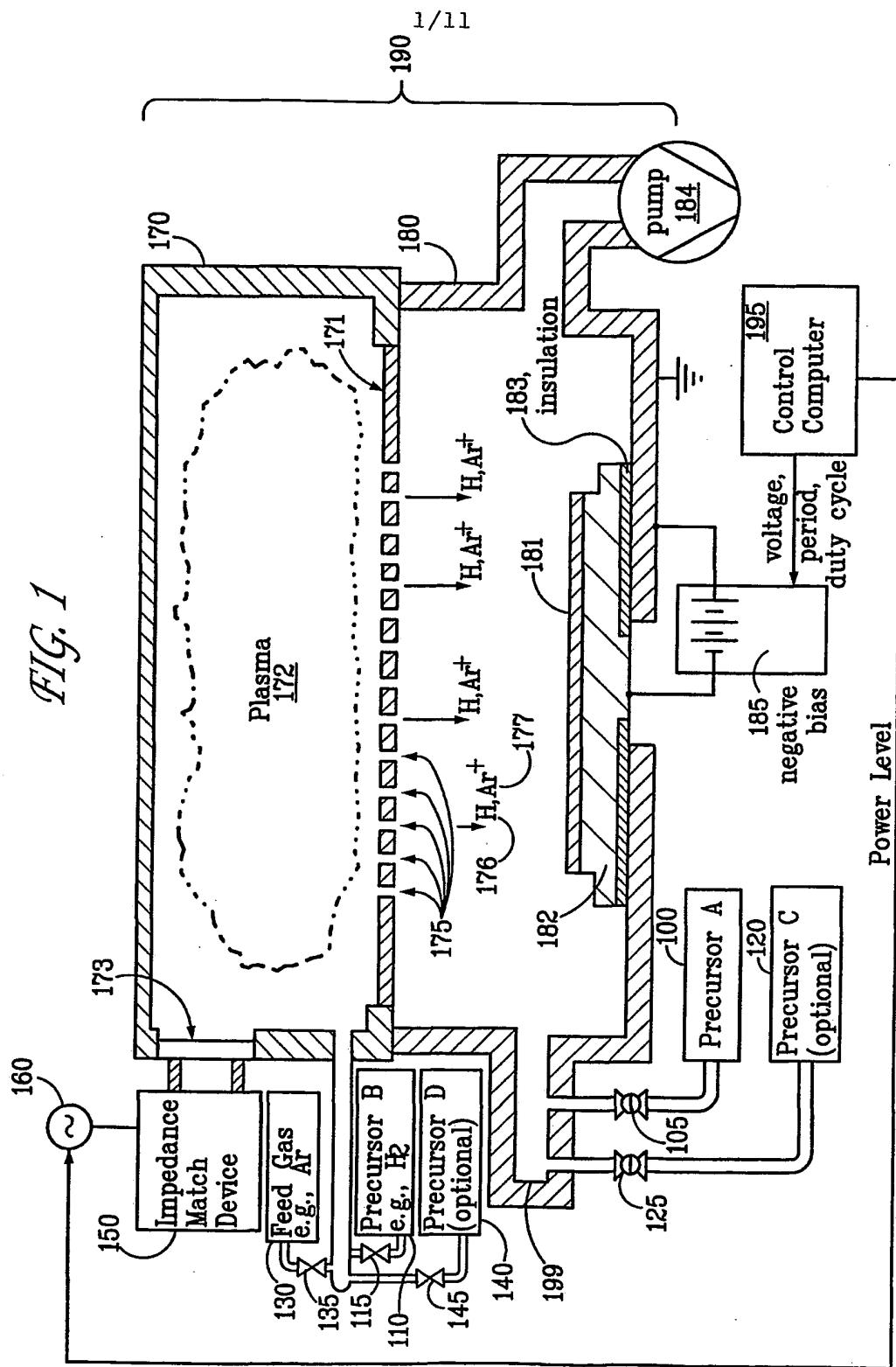
1        30.    The method of claim 28, further comprising exposing said  
2    substrate to said reactant gas while varying exposure of said substrate to said  
3    ions via said ion modulation.

1        31.    The method of claim 30, wherein said ion modulation is effected  
2    in a way selected from the group consisting of modulating an ion flux and  
3    modulating an ion energy.

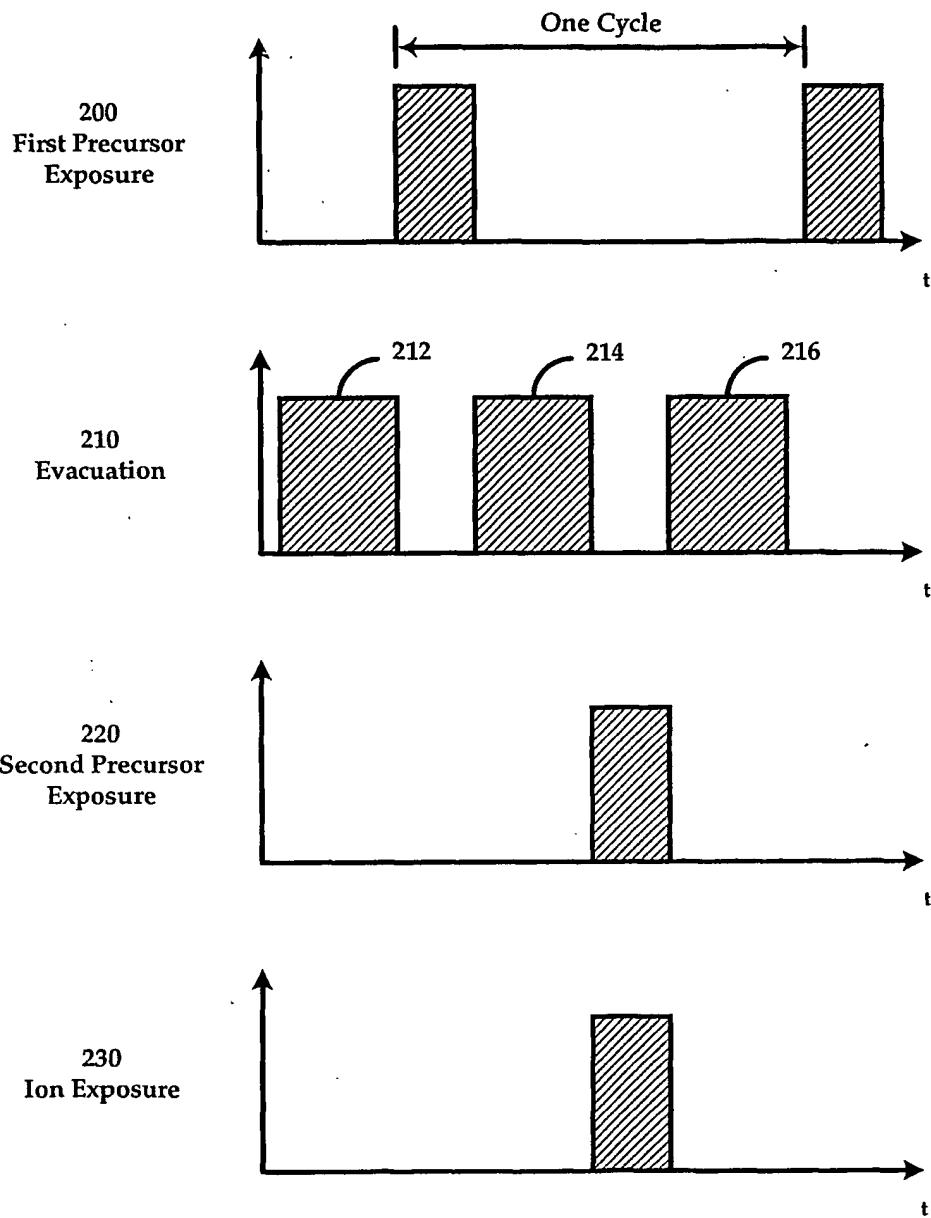
1        32.    The method of claim 31, wherein modulation in said ion flux is  
2    modulated in a way selected from the group consisting of modulating a flow  
3    of said ion generating feed gas, modulating a power of said plasma,  
4    mechanically occluding said ions, and modulating the relative movement  
5    between said plasma and said substrate.

1        33.    The method of claim 28, further comprising maintaining said  
2    substrate at a temperature of between about 25 °C to 350 °C.

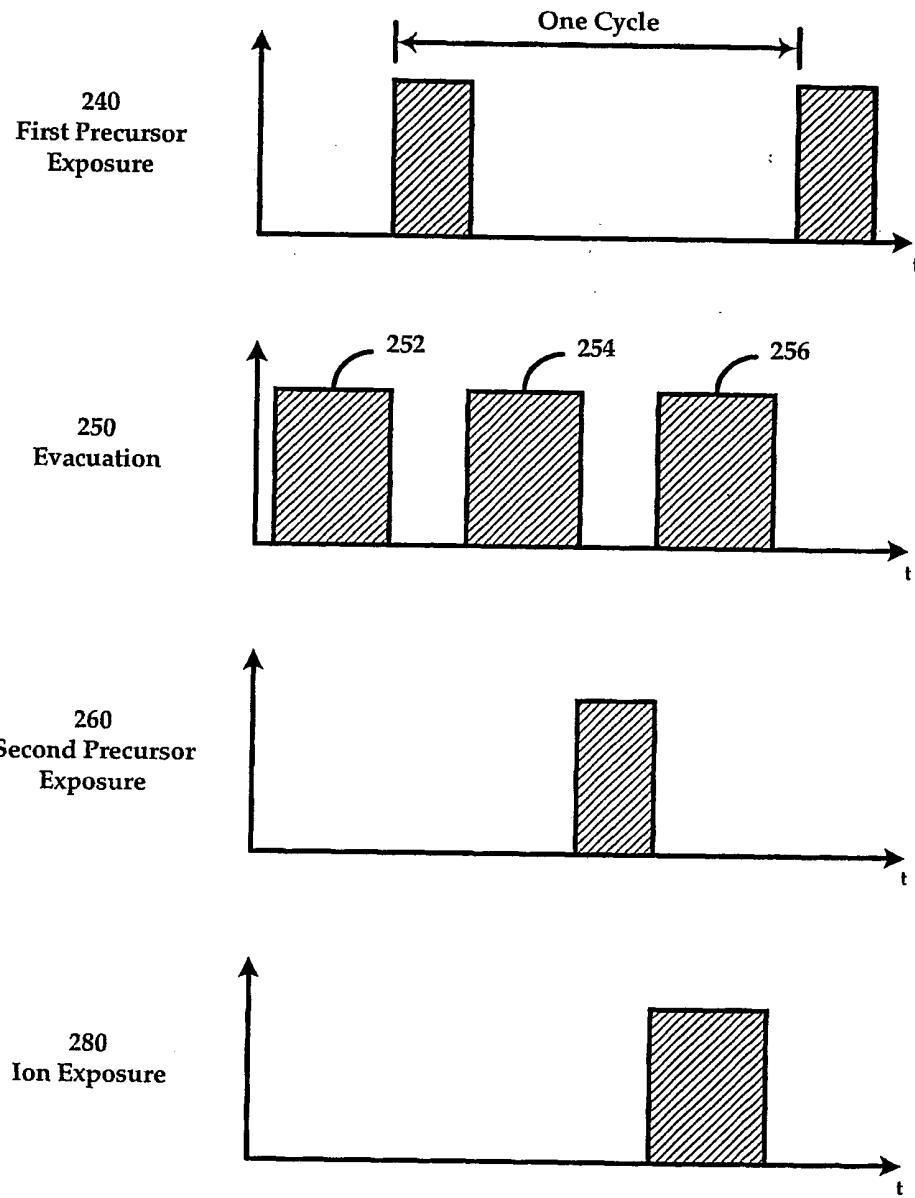
FIG. 1



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**Figure 2A**

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**Figure 2B**

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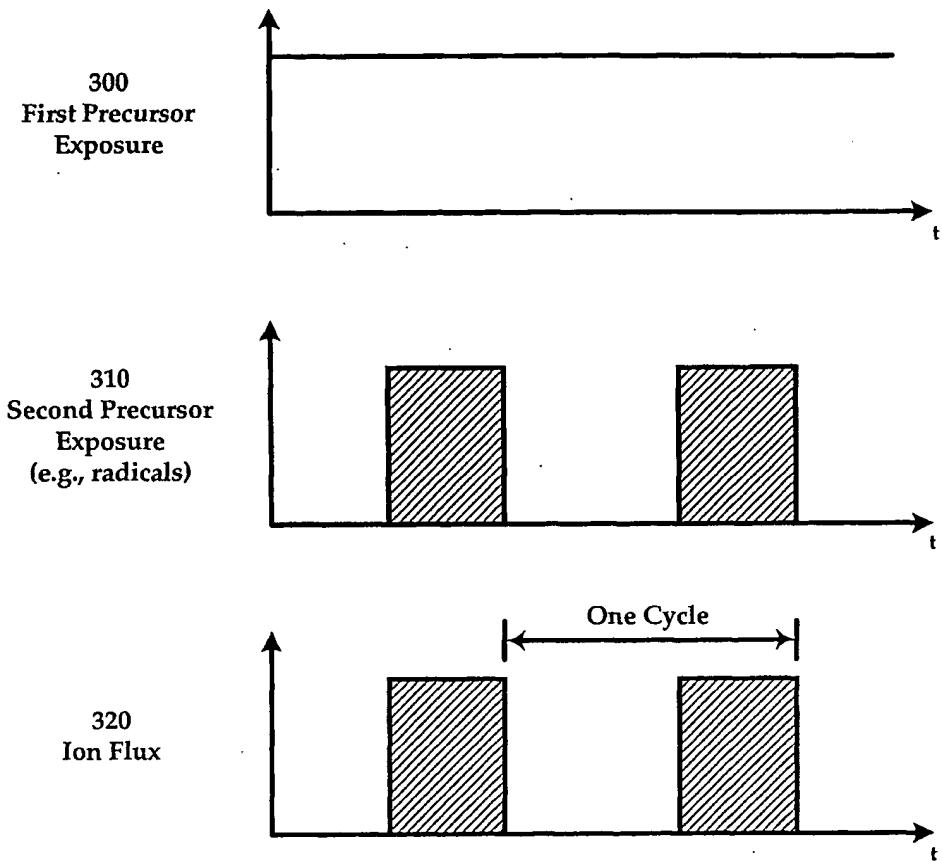


Figure 3A

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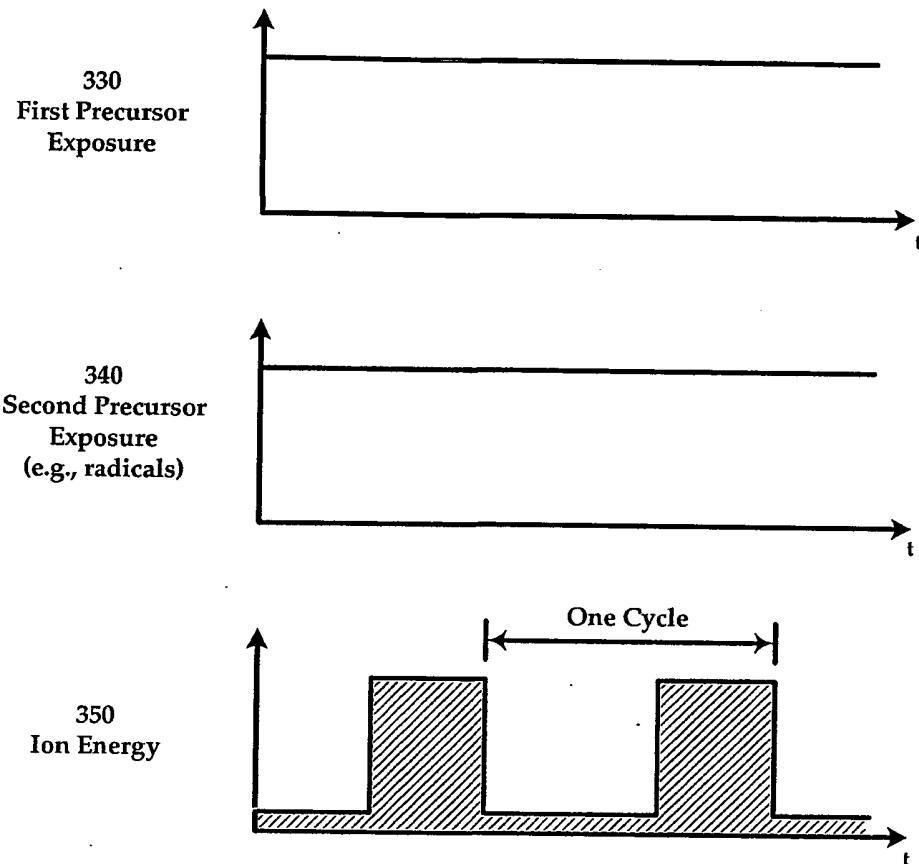
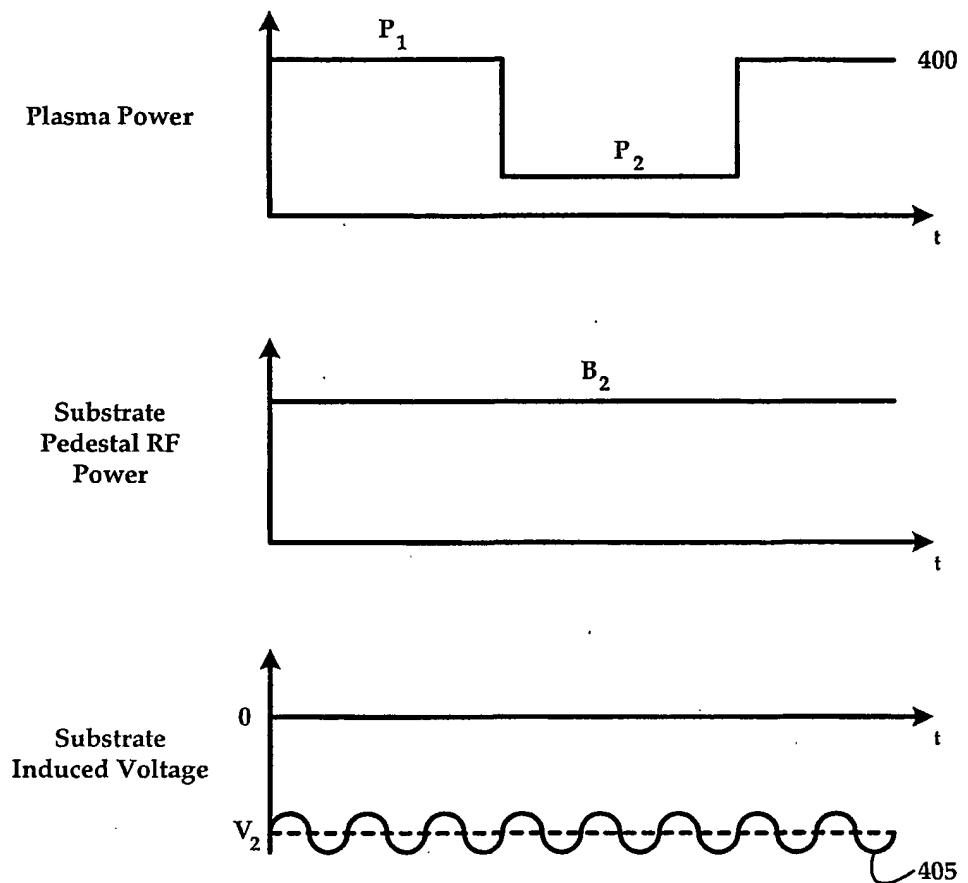


Figure 3B

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**Figure 4A**

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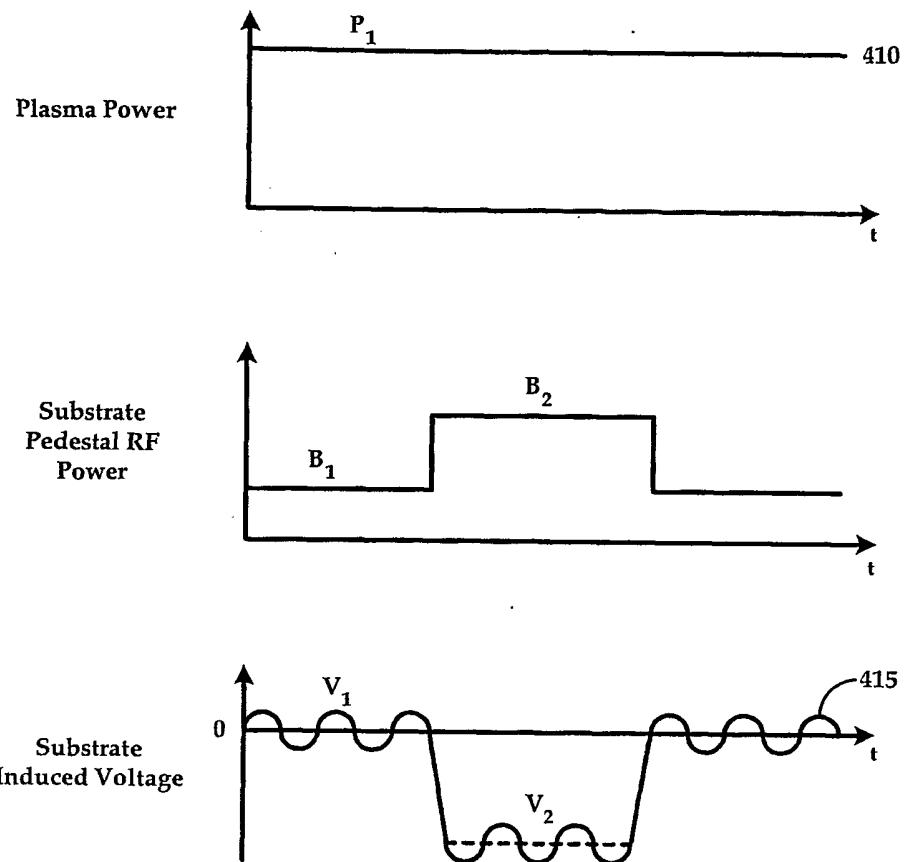
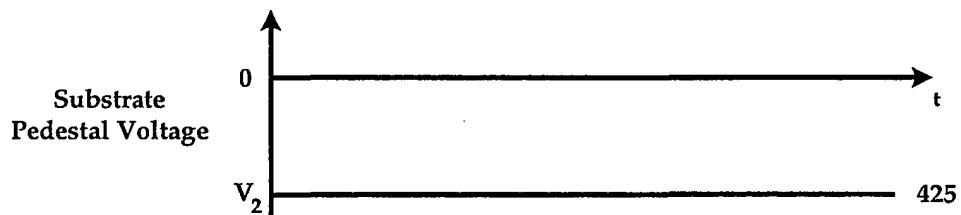
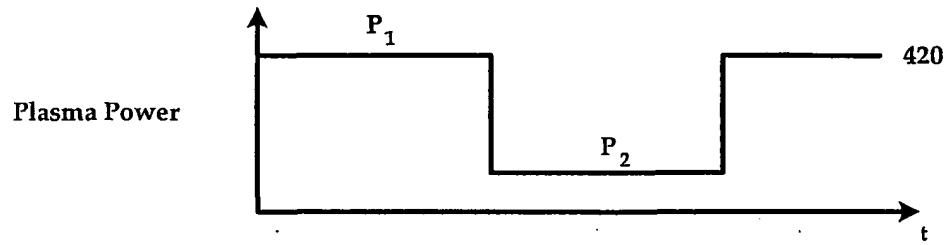
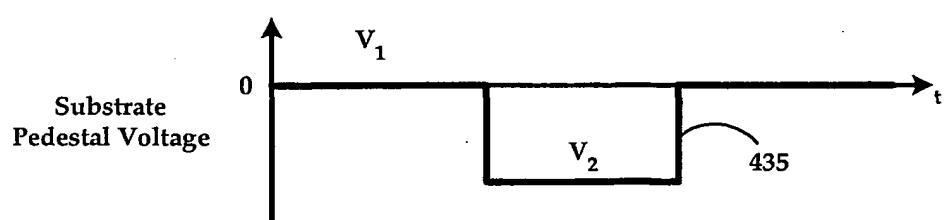
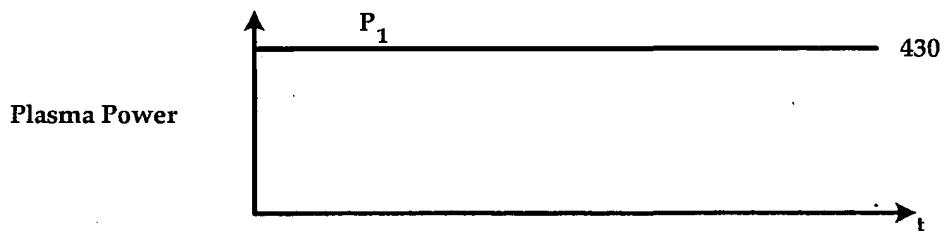


Figure 4B

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**Figure 4C**



**Figure 4D**

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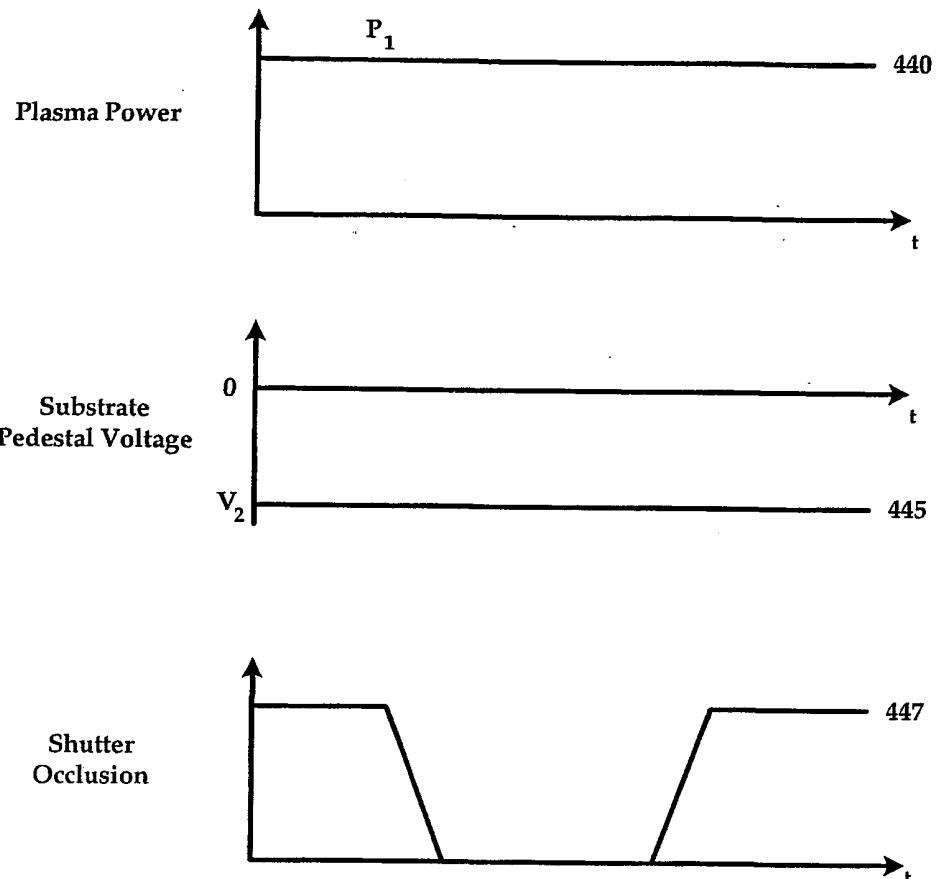
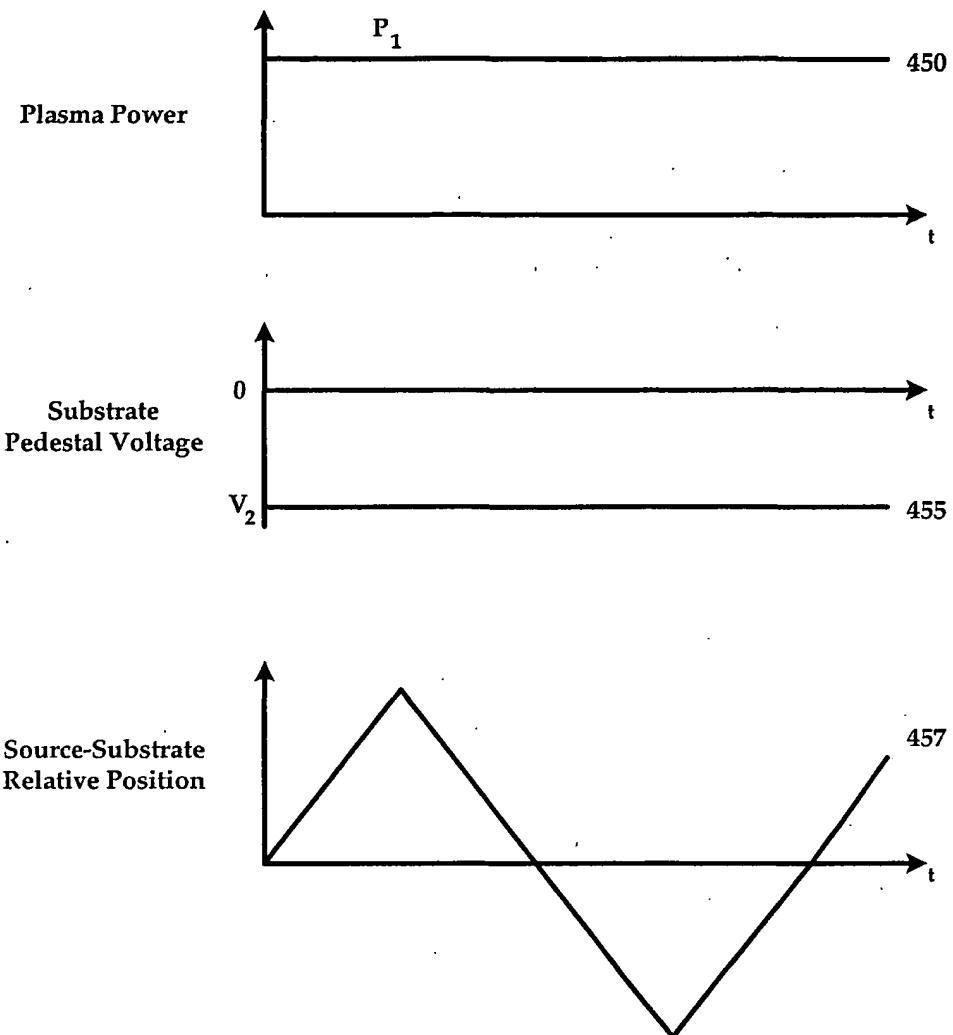


Figure 4E

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**Figure 4F**

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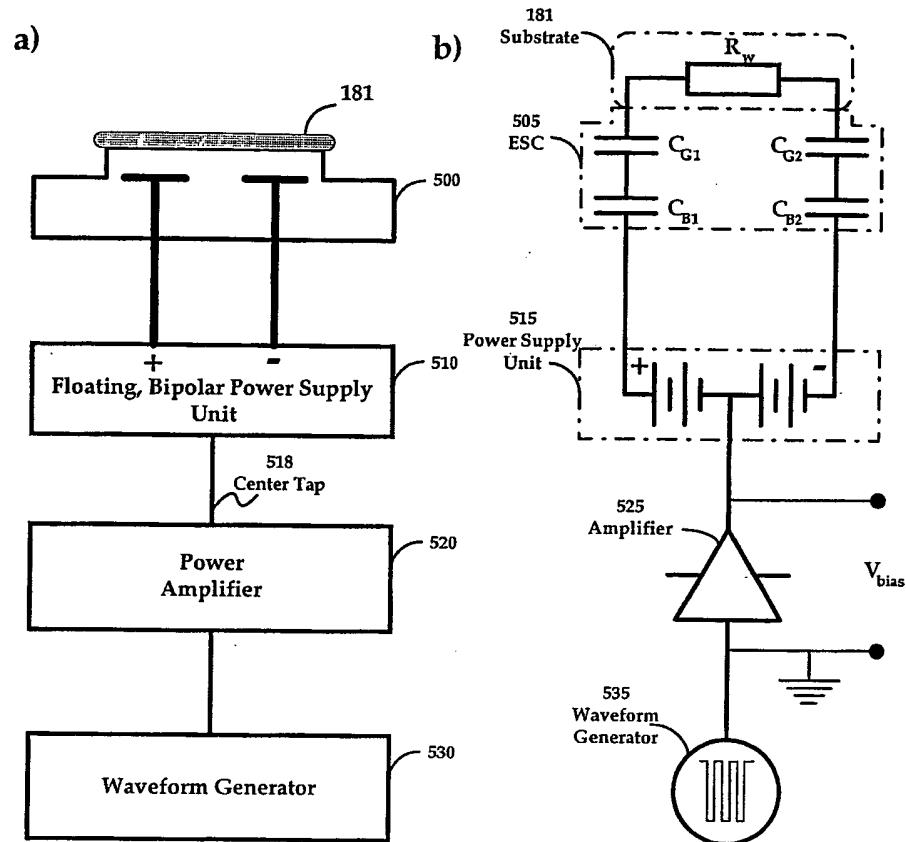


Figure  
5

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US01/50350

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : B05D 3/04; C23C 16/00, 16/44, 16/452, 16/455, 16/505, 16/511; C30B 25/00, 25/08, 25/14; H05H 1/24  
US CL : 427/561, 569, 570, 575. 248.1, 255.28, 255.5; 117/88, 92, 103, 105; 118/719, 723R, 723MW, 723I, 729

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Continuation Sheet

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,916,365 A (SHERMAN) 29 June 1999 (29.06.1999), abstract, figures 1-3, columns 5-6, and column 7, lines 13-26.	1-3, 16-22, 26
---		-----
Y		23-25, 27
X,P	US 6,200,893 B1 (SNEH) 13 March 2001 (13.03.2001), abstract, figure 1, columns 3-6, column 7, lines 1-25, column 8, lines 5-15, column 10, lines 35-67, and column 11, lines 1-11.	1, 2, 16-21
---		-----
Y,P		3, 22-27
X	US 4,401,054 A (MATSUO et al) 30 August 1983 (30.08.1983), abstract, figures 3 and 6, columns 5-7, column 8, lines 1-5, column 9, lines 39-56, column 10, lines 20-65, columns 11-12, column 14, lines 60-67, and column 15, lines 1-3 and 36-38.	4, 7-15
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Y	US 5,762,714 A (MOHN et al) 09 June 1998 (09.06.1998), column 2, lines 8-17.	5, 6, 23-25
Y	US 5,478,403 A (SHINAGAWA et al) 26 December 1995 (26.12.1995), column 7, lines 20-24.	24
		5, 6, 27

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"B" earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 11 March 2002 (11.03.2002)	Date of mailing of the international search report 04 APR 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized Officer Sylvie Beck Telephone No. (703) 308-0661

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US01/50350

**Continuation of B. FIELDS SEARCHED Item 1:**  
427/532, 533, 535, 561, 562, 564, 569, 570, 573, 575, 248.1, 250, 255.23, 255.28, 255.5; 117/84, 88, 89, 91, 92, 93, 98, 99, 100, 103, 105; 118/715, 719, 723R, 723MW, 723ME, 723I, 723IR, 728, 729

**Continuation of B. FIELDS SEARCHED Item 3:**

WEST electronic search, all databases.

search terms: ALD, ALE, atomic layer deposition, atomic layer epitaxy, plasma, ion, radical, showerhead, sequential CVD, and various combinations thereof.